Communications

Synthesis and Structural Characterization of an Imidazolium-Linked Cyclophane and the Silver Complex of an N-Heterocyclic Carbene-Linked Cyclophane

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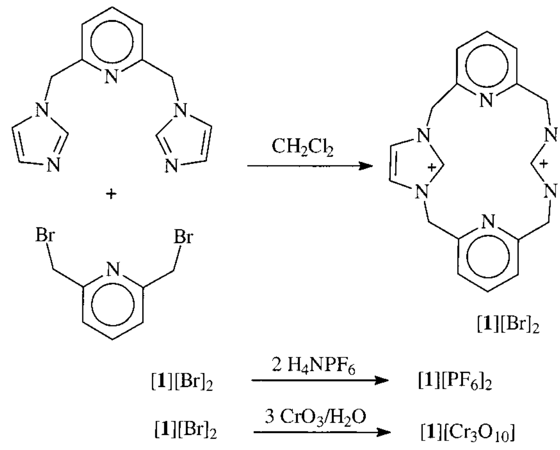
Summary: The synthesis and structural characterization of a dicationic imidazolium-linked cyclophane and a dimeric N-heterocyclic carbene complex are described.

The synthesis of transition-metal complexes of imidazol-2-ylidenes, also known as N-heterocyclic carbenes, was first pioneered by Öfele[1] and Wanzlick[2] in 1968 and is a very active area of research today.[3] The synthesis of free isolable N-heterocyclic carbenes and their complexation with transition metals were first reported by Arduengo in 1991.[4] It is not always convenient to synthesize complexes from free carbenes and transition metals. A recent advance is the use of silver bis(carbene) complexes as carbene transfer reagents.[5]

The chemistry of cyclophanes has been of interest for decades.[6] Much of this interest has been promoted by the utility of cyclophanes to act as molecular recognition reagents in host−guest chemical systems. Recently, two reports have appeared in the literature of imidazolium-linked cyclophanes.[7,8] However, N-heterocyclic carbene-linked cyclophanes have not been reported. The chemistry of these compounds would be extremely important because the carbene moieties could complex to transition and main-group metals, offering novel host−guest chemical systems. We are interested in developing the chemistry of carbene-linked cyclophanes that contain two pyridine rings linked by N-heterocyclic carbenes. This interest is complementary to our work involving macrocyclic ligands that can stabilize transition metals and main-group elements in unusual coordination numbers and/or oxidation states.[9] We report herein the synthesis and structural characterization of the dicationic imidazolium-linked cyclophane **1** and the dimeric silver N-heterocyclic carbene complex $[Ag_2(\mathbf{1})_2][PF_6]_2$ (**2**). Silver-complexed N-heterocyclic carbene-linked cyclophanes should be useful reagents in the synthesis of transition- and main-group-metal complexed N-heterocyclic carbene-linked cyclophanes.

Scheme 1



The synthesis of the cyclophanes $[\mathbf{1}][Br]_2$, $[\mathbf{1}][Cr_3O_{10}]$, and $[\mathbf{1}][PF_6]_2$ is outlined in Scheme 1. The 3 + 1 condensation reaction of 2,6-bis(imidazolmethyl)pyridine[10] and 2,6-bis(bromomethyl)pyridine in CH_2Cl_2 affords $[\mathbf{1}][Br]_2$ as an off-white solid in 50% yield. Treatment of an aqueous solution of $[\mathbf{1}][Br]_2$ with either 3 equiv of CrO_3 or 2 equiv of ammonium hexafluorophosphate affords $[\mathbf{1}][Cr_3O_{10}]$ and $[\mathbf{1}][PF_6]_2$ in 42% and 80% yields, respectively. The FAB-MS spectra obtained from $[\mathbf{1}][Br]_2$ and $[\mathbf{1}][PF_6]_2$ in nitrobenzyl alcohol matrices showed $[\mathbf{1}][Br]^+$ ($C_{20}H_{20}N_6Br$) at m/z 423 and $[\mathbf{1}][PF_6]^+$ ($C_{20}H_{20}N_6PF_6$) at m/z 489, respectively. The ^1H and ^{13}C NMR spectra (d_6-DMSO) for $[\mathbf{1}][Br]_2$, $[\mathbf{1}][PF_6]_2$, and $[\mathbf{1}][Cr_3O_{10}]$ are essentially identical and consistent with the proposed structure of **1**. Each of the ^1H NMR spectra

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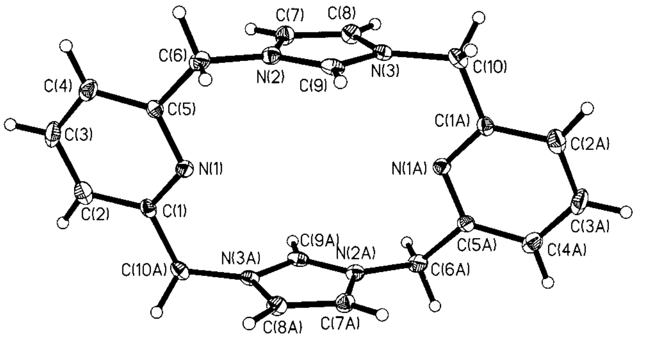


Figure 1. Molecular structure of the dicationic portion of $[\mathbf{1}][\mathrm{PF}_6]_2$ with thermal ellipsoids drawn at 30% probability.

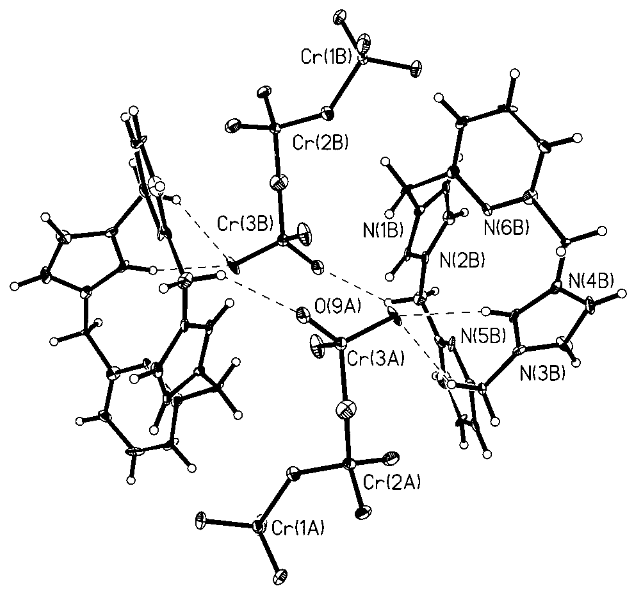


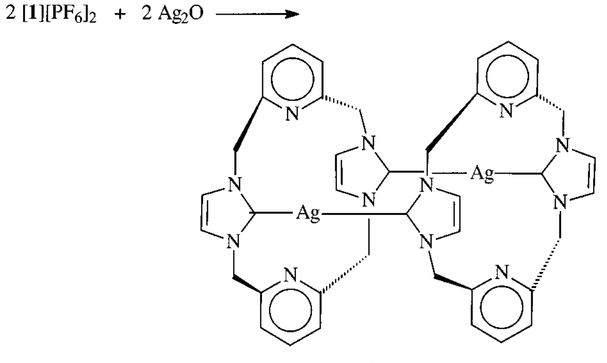
Figure 2. Thermal ellipsoid plot of two molecules of $[\mathbf{1}][\mathrm{Cr}_3\mathrm{O}_{10}]$, showing hydrogen bonding. Thermal ellipsoids are drawn at 30% probability.

consist of resonances at ca. δ 5.6 (s, 8 H, CH$_2$), 7.6 (d, 4 H, $J = 8$ Hz, *m*-pyridine), 7.6 (s, 4 H, NC*H*), 8.0 (tr, 2 H, $J = 8$ Hz, *p*-pyridine), and 9.0 (s, 2 H, $\mathrm{C}^+{-}H$).

Crystals of $[\mathbf{1}][\mathrm{PF}_6]_2$ and $[\mathbf{1}][\mathrm{Cr}_3\mathrm{O}_{10}]$ suitable for X-ray crystallography were obtained by slow evaporation of an acetonitrile solution of each complex.[11,12] The structure of the dicationic portion of $[\mathbf{1}][\mathrm{PF}_6]_2$ is illustrated in Figure 1. The thermal ellipsoid plot of two molecules of $[\mathbf{1}][\mathrm{Cr}_3\mathrm{O}_{10}]$ is illustrated in Figure 2. Compound $[\mathbf{1}][\mathrm{PF}_6]_2$ adopts a “staggered chair” conformation that is symmetrical about an inversion center. The planes formed by the imdazolium rings are parallel, as are the planes formed by the pyridine rings. In contrast, $[\mathbf{1}][\mathrm{Cr}_3\mathrm{O}_{10}]$ adopts a distorted asymmetric “eclipsed chair” conformation. The cyclophane $[\mathbf{1}][\mathrm{PF}_6]_2$ has an inner cavity that adopts the shape of a box with dimensions 5.1 Å (N1−N1A) and 4.8 Å (distance between the centroids of imidazolium rings). In contrast, $[\mathbf{1}][\mathrm{Cr}_3\mathrm{O}_{10}]$ has a slighty smaller inner cavity with dimensions 4.9 Å (N5−N6) and 4.5 Å (C1−C11).

Cyclophanes $[\mathbf{1}][\mathrm{PF}_6]_2$ and $[\mathbf{1}][\mathrm{Cr}_3\mathrm{O}_{10}]$ form hydrogen-bonded networks in the solid state.[13] The cyclophane $[\mathbf{1}][\mathrm{PF}_6]_2$ packs with intermolecular hydrogen-bonding interactions between fluorine atoms of the PF_6^- anions and the methylene hydrogen atoms (H- - -F = 2.47 Å, C- - -F = 3.47 Å, C−H- - -F = 107°) and the imidazolium hydrogen atoms (H- - -F = 2.50 Å, C- - -F = 3.20 Å, C−H- - -F = 136°) of the dicationic cyclophanes.The cyclophane $[\mathbf{1}][\mathrm{Cr}_3\mathrm{O}_{10}]$ packs with intermolecular hydrogen-bonding interactions between oxygen atoms of the $\mathrm{Cr}_3\mathrm{O}_{10}^{2-}$ anions and the methylene hydrogen atoms and the imidazolium hydrogen atoms of the dicationic cyclophanes. The H- - -O−Cr hydrogen-bonding interactions have distances that vary in the range of 2.41−2.55 Å (average 2.44 Å) and C−H- - -O bond angles that vary in the range of 131−155° (average 139°). The cyclophane $[\mathbf{1}][\mathrm{Cr}_3\mathrm{O}_{10}]$ has many more hydrogen-bonded interactions than $[\mathbf{1}][\mathrm{PF}_6]_2$, and we presume that this results in the irregular geometry of the dication portion of $[\mathbf{1}][\mathrm{Cr}_3\mathrm{O}_{10}]$. It is notable that the imidazolium rings in $[\mathbf{1}][\mathrm{PF}_6]_2$ are staggered but the imidazolium rings of $[\mathbf{1}][\mathrm{Cr}_3\mathrm{O}_{10}]$ are eclipsed. We attribute this to packing forces that are governed by the differences in counter-anions (two PF_6^- anions per dication versus one $\mathrm{Cr}_3\mathrm{O}_{10}^{2-}$ dianion per dication).

Treatment of the cyclophane $[\mathbf{1}][\mathrm{PF}_6]_2$ with Ag$_2$O in DMSO at 55 °C affords the silver N-heterocyclic carbene complex $[\mathrm{Ag}_2(\mathbf{1})_2][\mathrm{PF}_6]_2$ (**2**) (eq 1). Complex **2** dissolved in acetonitrile/H$_2$O (1:1) solution generates $\mathrm{Ag}[\mathbf{1}]^+$ ions at *m*/*z* 449/451 upon ESI-MS (C$_{20}$H$_{18}$N$_6$Ag; calculated *m*/*z* 449/451). Analysis of the isotopic pattern from the mass spectroscopy data indicates a monomeric structure for **2** in the gas phase. The ^{1}H NMR spectrum of **2** consists of resonances at ca. δ 5.2 (s, 16 H, CH$_2$), 7.0 (s, 8 H, NC*H*), 7.3 (d, 8 H, $J = 6$ Hz, *m*-pyridine), and 7.5 (tr, 4 H, $J = 8$ Hz, *p*-pyridine). These values are shifted upfield when compared to the same values obtained for the precursor $[\mathbf{1}][\mathrm{PF}_6]_2$. The most notable feature in the ^{1}H NMR spectrum for **2** is the absence of the resonances for the imidazolium protons at ca. 9 ppm. In the ^{13}C NMR spectrum for **2**, the imdazolium carbon atom appears as a broad peak at 183 ppm. This value is characteristic of a carbene moiety. The broadness can be attributed to the unresolved couplings between the



(1)

$[\mathbf{2}][\mathrm{PF}_6]_2$

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(11) Crystal data for $\mathrm{C}_{20}\mathrm{H}_{20}\mathrm{F}_{12}\mathrm{N}_6\mathrm{P}_2$ ($[\mathbf{1}][\mathrm{PF}_6]_2$): MW = 634.36, monoclinic, space group $P2_1/n$, $a = 11.046(7)$ Å, $b = 10.036(5)$ Å, $c = 11.919(7)$ Å, $\beta = 103.72(4)°$, $V = 1283.6(12)$ Å^3, $Z = 2$, $D_c = 1.641$ Mg/m^3, $\mu = 0.280$ mm^{-1}, $T = 121$ K. Refinement for data with $I > 2\sigma(I)$ (2261 reflections) gave R1(F) = 0.0438 and wR2(F^2) = 0.0835 for all data.

(12) Crystal data for $\mathrm{C}_{20}\mathrm{H}_{20}\mathrm{Cr}_3\mathrm{N}_6\mathrm{O}_{10}$ ($[\mathbf{1}][\mathrm{Cr}_3\mathrm{O}_{10}{}^2]$): MW = 660.42, monoclinic, space group $P2_1/n$, $a = 9.264(6)$ Å, $b = 9.786(4)$ Å, $c = 27.974(13)$ Å, $\beta = 92.42(5)°$, $V = 2534(2)$ Å^3, $Z = 4$, $D_c = 1.731$ Mg/m^3, $\mu = 1.330$ mm^{-1}, $T = 133$ K. Refinement for data with $I > 2\sigma(I)$ (2261 reflections) gave R1(F) = 0.0901 and wR2(F^2) = 0.2497 for all data.

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carbon and the ^{107}Ag and ^{109}Ag nuclei. Similar observations have been reported and explained in terms of fluxional behavior.[14]

Crystals suitable for X-ray crystallography of **2** were obtained by slow evaporation of an acetonitrile solution of the complex.[15] Complex **2** crystallizes as a silver-bridged dimer that is symmetric about an inversion center, and the structure of the silver−cyclophane portion of **2** with selected bond distances and angles is illustrated in Figure 3. The geometry of the cyclophane portions of **2** varies only slightly from the same parameters for the precursor **1**. The N-heterocyclic carbenes are eclipsed, and each is bonded to a silver atom (C1−Ag = 2.096(9) Å) which is also bonded to another carbene carbon atom (C11−Ag = 2.084(9) Å) of an adjacent cyclophane molecule. The geometry at the Ag atoms is nearly linear, with a C1−Ag−C11 bond angle of 171.3(3)°. These values are quite normal when compared to the same values reported for other silver−bis(carbene) complexes.[5a,b16]

In conclusion, we have synthesized the pyridine-containing cyclophane [**1**][Br]$_2$ by a 3 + 1 condensation reaction. The two bromide anions were exchanged with two PF_6^- anions to yield [**1**][PF$_6$]$_2$ or with one $Cr_3O_{10}^{2-}$ dianion to yield [**1**][Cr$_3$O$_{10}$]. The structures of [**1**][PF$_6$]$_2$ and [**1**][Cr$_3$O$_{10}$] were confirmed by X-ray crystallography. The cyclophane [**1**][PF$_6$]$_2$ reacts with Ag$_2$O to afford the silver carbene complex [Ag$_2$(**1**)$_2$][PF$_6$]$_2$ (**2**). Complex **2** is the first example of a *carbene*-linked cyclophane. We are exploring the carbene transfer chemistry of **2** with other transition metals.

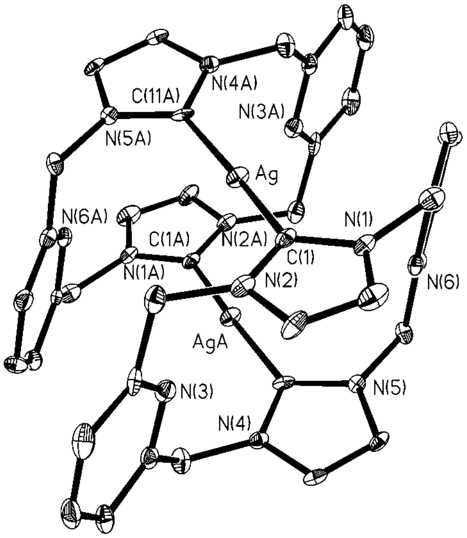

Figure 3. Crystal structure of the dicationic portion of [Ag$_2$(**1**)$_2$][PF$_6$]$_2$ (**2**). Thermal ellipsoids are drawn at 30% probability. Hydrogen atoms have been omitted for clarity.

Acknowledgment. We thank the University of Akron and the Ohio Board of Regents for financial support. We thank Kathleen M. Wollyung for experimental assistance in the acquisition of the mass spectra.

Supporting Information Available: Text giving detailed experimental procedures for the syntheses of [**1**][Br]$_2$, [**1**][PF$_6$]$_2$, [**1**][Cr$_3$O$_{10}$], and [Ag$_2$(**1**)$_2$][PF$_6$]$_2$ (**2**) and tables giving X-ray crystallographic data for [**1**][PF$_6$]$_2$, [**1**][Cr$_3$O$_{10}$], and [Ag$_2$(**1**)$_2$]-[PF$_6$]$_2$ (**2**). This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Crystal data for $C_{40}H_{36}F_{12}N_{12}P_2Ag_2$ (**2**): MW = 1190.48, triclinic, space group $P\bar{1}$, $a = 9.788(3)$ Å, $b = 10.212(3)$ Å, $c = 11.685(4)$ Å, $\alpha = 75.180(6)°$, $\beta = 86.639(6)°$, $\gamma = 72.884(6)°$, $V = 1079.0(6)$ Å^3, $Z = 2$, $D_c = 1.832$ Mg/m^3, $\mu = 1.082$ mm^{-1}, $T = 150$ K. Refinement for data with $I > 2\sigma(I)$ (2261 reflections) gave R1(F) = 0.0721 and wR2(F^2) = 0.1993 for all data.

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